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Synthetic and spectral studies of complexing behaviour of nitrito complex of 4 [(N-4-Di ethylamino-2methyl benzalidine) amino] antipyrine.

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Abstract

Pyrazolones have been reported to be potential extractants as well as powerful drugs, their varied chemical and physical properties. Trivalent lanthanides behave as hard acids and thus are expected to form stronger stable complexes with ligands having oxygen or N-donor atoms. Lanthanide (III) Nitrate and double the amount of ligand (4[(N-4-Diethyl amino 2-methyl benzalidene) amino] antipyrine) $C_{23}H_{28}N_4O$ are used for formation of complexes. The characterization of the newly synthesized complexes by molar conductance, molecular weight, magnetic susceptibility, infrared and electronic spectroscopy.

Keywords: Pyrazolones, Lanthanide Nitrates,molar conductance, molecular weight, magnetic susceptibility, infrared and electronic spectroscopy.

INTRODUCTION

Pyrazolones have been reported to be potential extractants[1-5] as well as powerful drugs[6], their varied chemical and physical properties such as high extraction efficiency, quantitative extraction at low pH, high selectivity and ease of stripping have led to their application in a number of industrial processes[7].

Trivalent lanthanides behave as hard acids and thus are expected to form stronger stable complexes with ligands having oxygen or N-donor atoms.

The Lanthanide (III) nitrates form deep colored complexes with the Schiff base. The prime object of the present work has therefore been to synthesize new schiff bases derived from 4-aminoantipyrine and Isolation of solid complexes of $LnNO_3$ (Ln=La, Pr, Nd, Sm, Gd, Tb and Dy) with these schiff base and Characterization of the newly synthesized complexes by molar conductance, molecular weight magnetic susceptibility, infrared and electronic spectroscopy.

MATERIALS

1. Lanthanide nitrates were procured from Rare Earth Products Ltd.Udoyg Mandal Kerala (India) and were used without further purification.
2. 4[(N-4-Diethyl amino-2methyl benzalidene) amino] antipyrine (DAMBAAP) $C_{23}H_{28}N_4O$ by condensation of ethanolic solutions of 4-Amino antipyrine and 2- methyl-4, N, N- diethyl amino benzaldihyde in unimoler ration. The yield of Lewis base is about 80%.

Preparation and isolation of the complexes

The corresponding lanthanide (III) nitrate (2 mmol) and double the amount of ligand was dissolved separately in hot methanol (20 ml each). The solution was thoroughly mixed and refluxed for about 3 hrs. After completion of the reaction the resulting solution of the nitrate complex was concentrated to half of its volume and to this diethyl-ether (25 ml) was added with vigorous stirring where upon the complex separated out. The finely divided solid mass washed with ethanol and finally washed with diethyl-ether and collected. All these complexes were dried in vacuo over P_4O_{10}.

Characterization, Identification and Conformation of structures of the complexes

Lanthanide salts reacts with 4 [(N-4-diethylamino 2-methyl benzalidene) amino] antipyrine ($C_{23}H_{28}N_4O$), resulting complexes of the general composition $Ln(NO_3)_3.2(C_{23}H_{28}N_4O)$ where Ln=La, Pr, Nd, Sm, Gd, Tb or Dy. Chemical analysis of the isolated compounds is given in Table 1.

Complexes are stable under ordinary conditions and can be kept for a sufficient long time without decomposition. Complexes are soluble in acetone, alcohol, acetonitrile and nitrobenzene as well as in dimethyl formamide and dimethyl sulfoxide. On heating the complexes up to 120-130^{0}C, no changes in loss in weight of the complexes are noticed showing the absence of Lattice or coordinated held water molecule.Molar conductance of the complexes in nitrobenzene shows their non electrolytic nature.

The magnetic susceptibility measurements were made by Gouy's method[8-9] using a semi-micro Mettler balance and electromagnetic field of 8.5 x 10^3 Gauss. All the observations are made at room temperature.

The magnetic moment values observed in the present studies are given in Table 2, show that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons However all other tripositive Lanthanide ions are paramagnetic due to the presence of 4f electrons, which are effectively shielded by $5s^2$ $5p^6$ electrons.

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Table 1.Analytical, conductivity and molecular weight data of lanthanide(III) nitrate complexes of 4[N-4-Diethyl amino-2-methyl-benzalidene amino] antipyrine ($C_{23}H_{28}N_4O$)

S. No.	Complex	(Found) calc. %				Ω M (ohm $^{-1}$ cm^2 mole^{-1})	Electrolytic nature	Average Mol. Wt.	Formula weight
		Metal	C	H	N				
1	$La(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	12.90 (12.90)	51.26 (51.06)	5.20 (5.10)	14.30 (14.20)	4.6	Non-electrolyte	1082	1076.9
2	$Pr(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	13.06 (13.0)	50.16 (50.0)	5.19 (5.02)	14.27 (14.07)	5.3	Non-electrolyte	1085	1078.9
3	$Nd(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	13.33 (13.20)	51.06 (51.0)	5.17 (5.02)	14.23 (14.03)	5.80	Non-electrolyte	1088	1082.2
4	$Sm(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	13.82 (13.70)	50.72 (50.60)	5.15 (5.03)	14.15 (14.02)	4.4	Non-electrolyte	1096	1088.4
5	$Gd(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	14.36 (40.20)	50.40 (50.30)	5.11 (5.0)	14.06 (13.95)	4.0	Non-electrolyte	1090	1095.3
6	$Tb(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	14.49 (14.32)	50.32 50.20)	5.11 (5.02)	14.40 (14.20)	6.2	Non-electrolyte	1099	1096.9
7	$Dy(NO_3)_3.2$ ($C_{23}H_{28}N_4O$)	14.77 (40.60)	50.16 (50.0)	5.09 (4.92)	13.99 (13.80)	7.10	Non-electrolyte	1110	1100.5

Sl. No	Ln^{3+}	Theoretical		
		Hund	Van Vleek	$R_2(SO_4)_3.8H_2O$
1	La	0.00	0.00	0.00
2	Pr	3.60	3.62	3.48
3	Nd	3.62	3.68	3.52
4	Sm	0.84	1.55	1.53
5	Gd	7.94	7.94	7.81
6	Tb	9.70	9.70	9.40
7	Dy	10.60	10.60	10.30

(I) $Ln(C_{23}H_{28}N_4O)_2(NO_3)_3$

(II) Ln = La, Pr, Nd, Sm, Gd, Tb, Dy

These complexes show a little deviation from the Van Vleck values[10] although they obey simple curie equation. This was to be expected as the crystal field splitting of the f- orbitals was of the order of 100 cm^{-1} a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate[11-16] levels have been split by the crystal field.

I.R. studies of the complexes:

The assignments of the IR- absorption frequencies of the synthesized compound and their complexes have been made by comparing their spectra with allied compounds like pyrazoles[17] mono substituted benzene ring[18] antipyrine, 4 –amino antipyrine [19-23] substituted 4- amino antipyrine [24-29]. In all the complexes carbonyl and azomethine group frequencies considerably reduced showing their involvement in chelation. In the present ligands Carbonyl absorption frequency occurs in the region (1620-1600cm^{-1}) in complexes this absorption frequency suffers a negative shift showing it involvement in chelation. The high negative shift in the carbonyl frequency may be attributed to the greater flow of electrons from the carbonyl group to the lanthanide (III) atom due to greater delocalization of positive charge on the nitrogen atom.

Another important band occurs in the range1600-1605 cm^{-1} attributed to υ(C=N) mode. In spectra of all the complexes this band is shifted to lower wave number and appears at 1570-1500 cm^{-1} respectively indicating the involvement of N-atom of the azomethine group in coordination[30]. These observations are in conformity with the earlier reported work on lanthanide (III) and dioxouranium (VI) complexes of schiff bases obtained from 4- amino antipyrine and hydroxy aldehydes[31].Five membered heteroaromatic compounds are found to give two strong bands near 1560 and 1490 cm^{-1} which are considered to be characteristic of five membered.Several other absorptions associated with C-H out-of-plane deformation modes appear in the range 920-720 cm^{-1} in the present ligands.

In the far infrared region, an absorption at ca. 660 cm^{-1} has been assigned to C=O in-Plane bending in the free ligands [32-34]. This shows a positive shift on complexation. Other absorptions given in Tables 5.1-5.9 do not show any significant change on complexation. Some new medium and weak bands are observed in the far infrared range 430-380 cm^{-1} in these complexes where the ligands have no absorptions vibration. These new non ligands bands are assigned to υ (Ln-0) and υ (Ln-N) modes observed for several other lanthanide (III) complexes [35-38].

For lanthanide (III) nitrate complexes the occurrence of two strong absorption at ~ 1525 – 1480 cm^{-1} and 1320 – 1285 cm^{-1} region is attributed to υ_4 and υ_1 modes of vibration of the covalently bonded nitrate group respectively suggesting that the nitrate groups lie inside the coordination sphere.

Since according to Lever *et al.*[39] bidentate coordination involves a greater distortion from D_{3h} symmetry than unidentate coordination therefore, bidentate complexes should show a large

separation of ($\upsilon_1 + \upsilon_4$). Nevertheless we have tried to apply this method to the present lanthanide (III) nitrate complexes of Schiff bases. A separation of ca. 55-30 cm^{-1} in the combination bands in the 1800-1700 cm^{-1} region concludes the bidentate nitrate coordination.

Electronic Spectral studies of Lanthanide Complexes:

The electronic spectra of Pr (III), Nd (III), Sm (III) and Dy (III) complexes show bands at lower energies as compared to those in the aqua metal ions [40]. This may be attributed to lowering of the interelectronic repulsion parameter on complexation [41].

In the UV- region of the electronic spectra of the complexes an intense band appears at 280nm due to the ($\pi - \pi^*$) transition. The 4f transitions are normally forbidden but are followed when degeneracy in the 4f orbital is lifted due to external crystal field [42, 43]. The spectra show a shift of the band towards lower energy compared with those of the aqua ions owing to nephelauxetic effect [44]. The bonding parameter ($b_{1/2}$) and the covalence parameter (β) are less than unity while sinhas parameter (δ) is positive indicating a moderate covalent character for the bond between [45]. The metals and ligands and

$$\bar{\beta} = \frac{\upsilon\,(complex)}{\upsilon\,(aquo)}\,;\; b_{\frac{1}{2}} = \left[\frac{1}{2}\,\left(1-\bar{\beta}\right)\right]^{\frac{1}{2}}$$

$$\delta = \frac{100\left(1-\bar{\beta}\right)}{\beta}$$

The hypersensitive bands of the Nd (III) complex resemble that of nine and eight coordinate complexes reported by Karrakar[45] suggesting a coordination number of nine and eight around the metal ion in the complexes[46-58].

Thermal studies on the Lanthanide Complexes

The thermal behavior of Lanthanide complexes of Schiff bases, viz, 4[N-4-(Diethyl amino-2-methylbenzalidene) amino] antipyrine ($C_{23}H_{28}N_4O$) have been reported. Pyrolysis properties show no loss in weight of Lanthanons nitrato complexes.

On the basis of above studies the following structure of the complexes have been assigned:

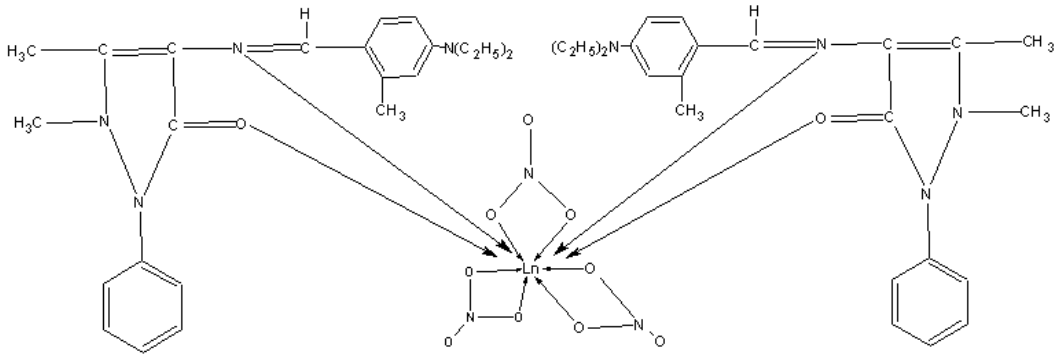

Fig 1. Structure of lanthanide (III) nitrates complexes of 4[(N-4-Diethyl amino-2-methyl-benzalidene) amino] antipyrine ($C_{23}H_{28}N_4O$)

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